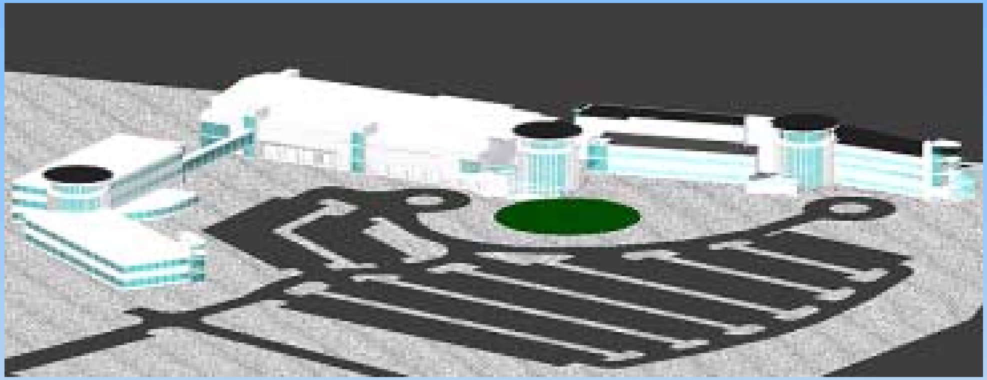
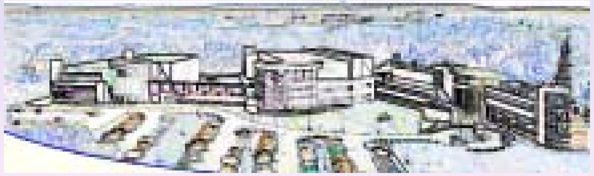
UNIVERSITY AT ALBANY
STATE UNIVERSITY OF NEW YORK

Feasibility of a SOFC Stack Integrated Optical Chemical Sensor



Michael A. Carpenter
School of NanoSciences and NanoEngineering
University at Albany, Albany, NY 12203



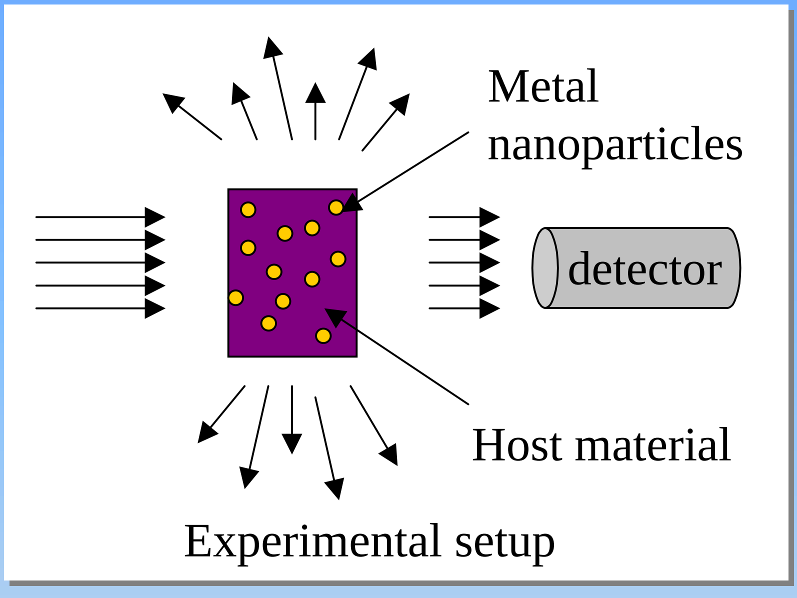
Outline

- Sensor Introduction and Material Set Properties
- Deposition
- Off-line optical interrogation
- Characterization
- Testing
- Theory
- Conclusions
- Future Work

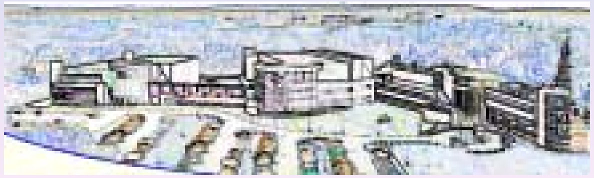
Surface Plasmon Resonance band Based Sensor for SOFC

- **Material set is stack integratable**
  - **YSZ matrix with embedded Pd, Au, Pt nanoparticles**
- **Monitor SPR changes as function of H_2, H_2S & CO and temperature**

- **All optical technique; intrinsically safe**
- **Material set is also compatible with Vision 21 initiatives**



Stack Operating Temperature (°C)
600-1000



Optical Properties of Metals

UNIVERSITY AT ALBANY
STATE UNIVERSITY OF NEW YORK

- **Drude theory alone is not sufficient to predict optical properties of metals, need to add in Lorentz oscillators for bound electrons**

$$\varepsilon = 1 - \underbrace{\frac{\omega_{pe}^2}{\omega^2 + i\gamma_e\omega}}_{\textbf{free electrons}} + \underbrace{\sum_j \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 - i\gamma_j\omega}}_{\textbf{bound electrons}}$$

ε: dielectric function V: volume of the particle

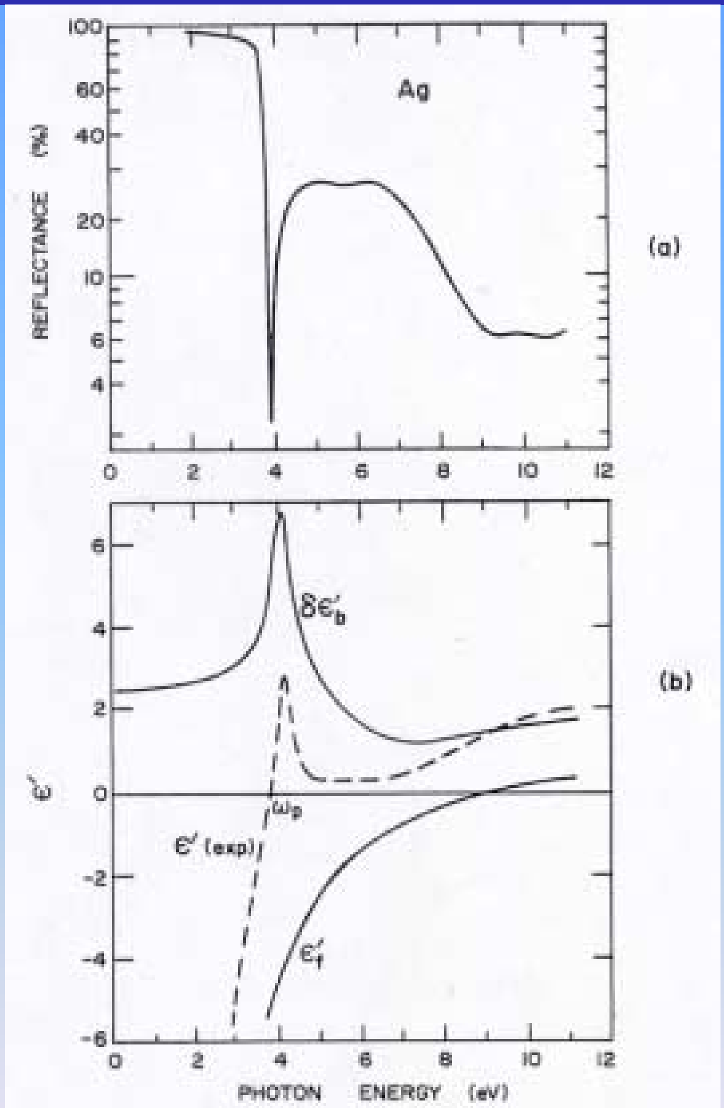
γ: damping factor q,κ: shape factors

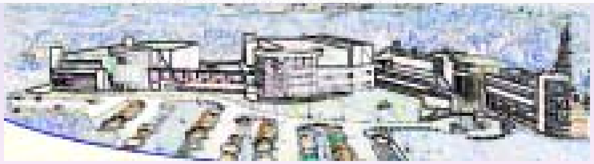
ω_p: plasma frequency k: wavenumber

ω_j: resonant frequency of bound electrons

- ***The real portion, (free electrons) of the dielectric function for metal nanoparticles takes negative values above certain wavelengths***
- ***Plasmon resonance shifted to higher wavelengths(lower energy)***

Bohren and Huffman



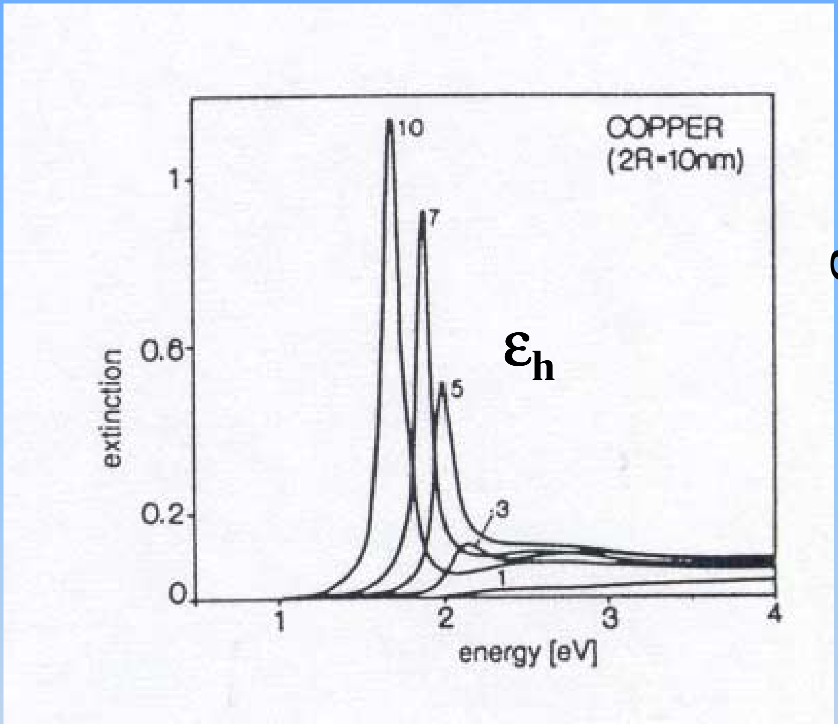


Immersion Spectroscopy

- **SPR bands can be enhanced or shifted to lower energies by embedding nanoparticles in an oxide matrix**

$$\alpha = \frac{V}{3q}\left\{\frac{\varepsilon_m - \varepsilon_h}{\varepsilon_m + \kappa\varepsilon_h}\right\}$$

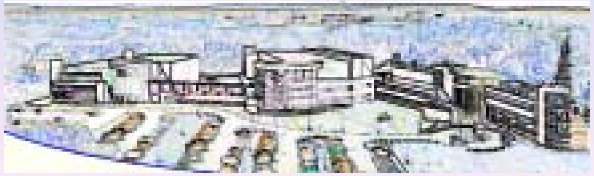
Polarizability (α) of a particle (ε_m) of arbitrary shape in host medium (ε_h), q and κ are shape factors:



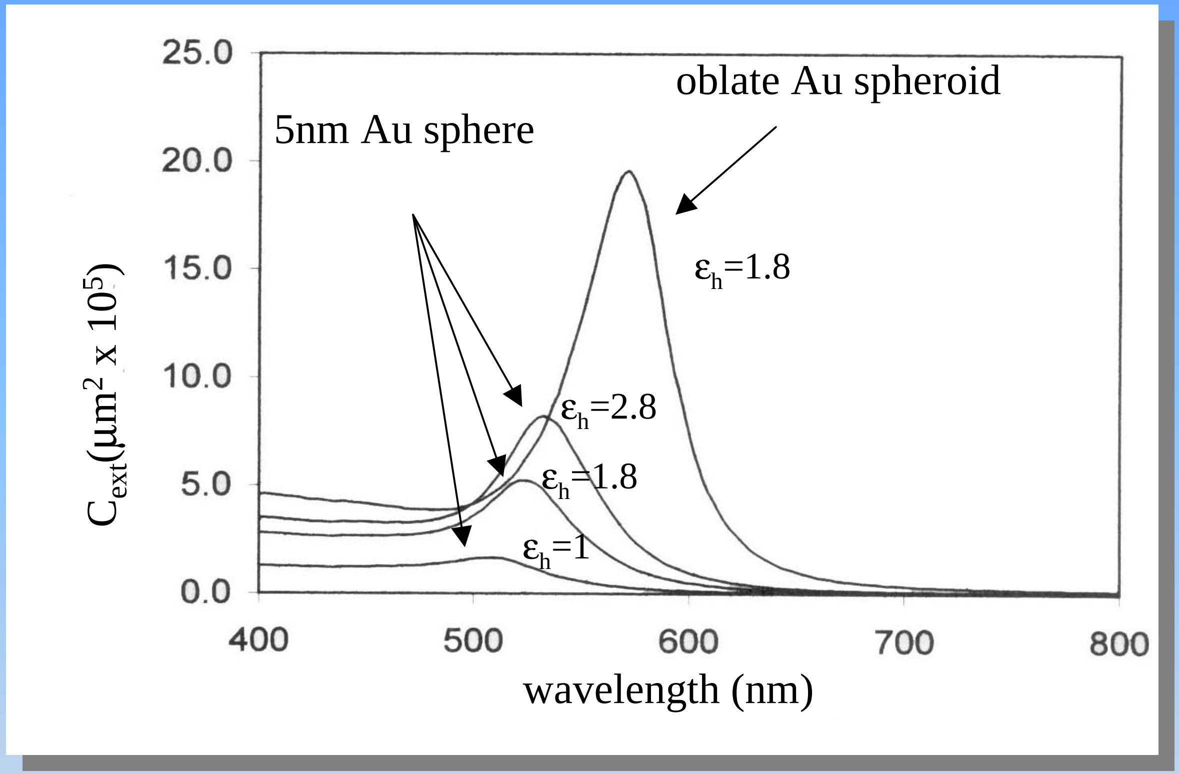
Kreibig and Vollmer

Extinction cross section

$$C_{ext} = k\,\mathrm{Im}\{\alpha\} + \frac{k^4}{6\pi}|\alpha|^2$$

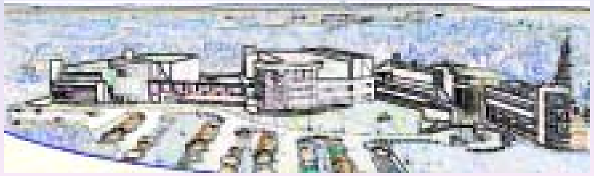


SPR and Shape Dependence



D. L. Feldheim, C. A. Foss, 2002

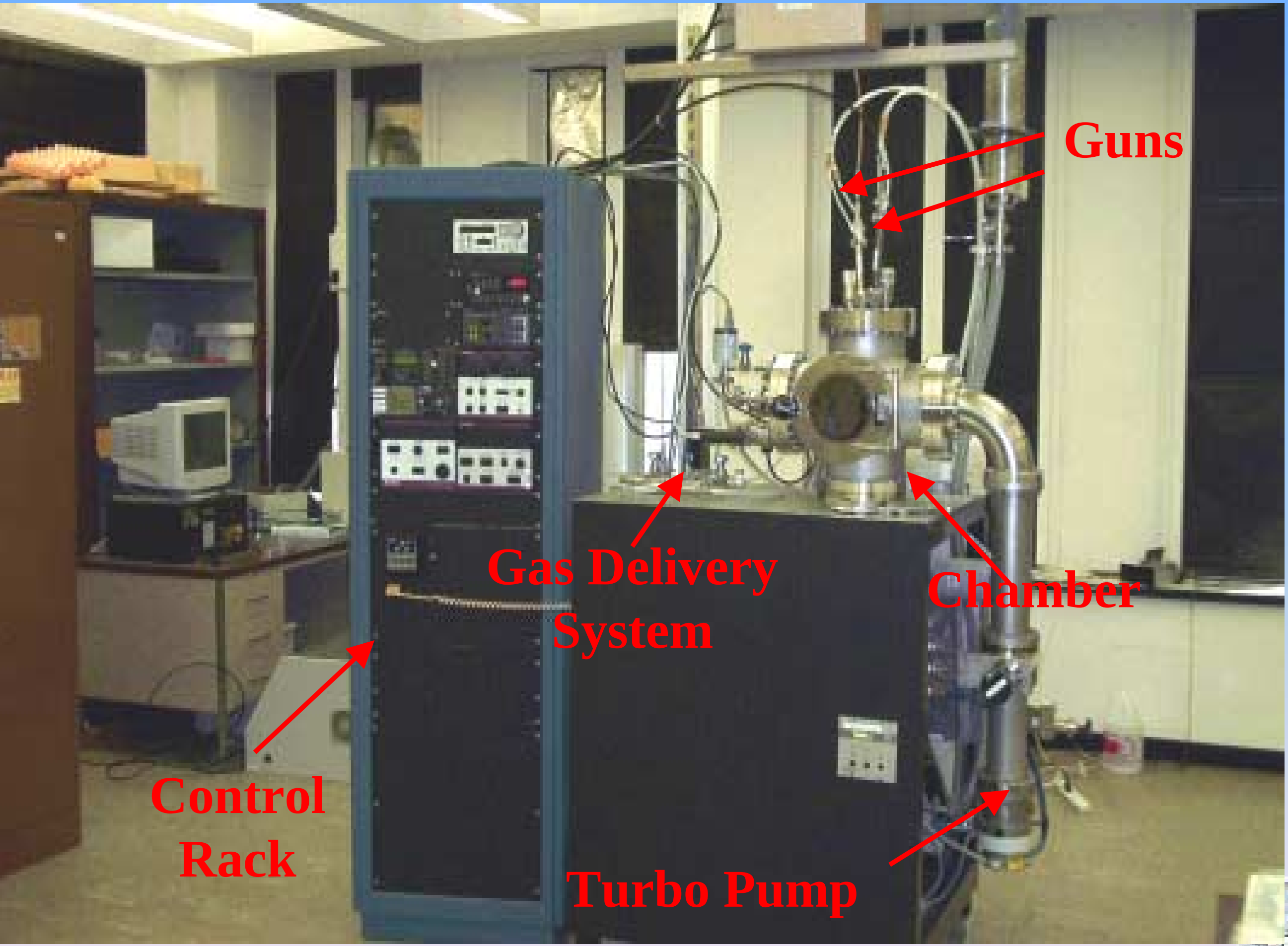
- ***The plasmon resonance extinction maximum can be shifted by changing the shape and/or the environment of the metal nanoparticle***
- ***Will also be sensitive to the surrounding chemical environment***



University at Albany
State University of New York

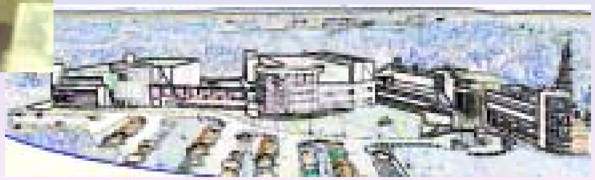
Physical Vapor Deposition

Dual Target Confocal PVD System

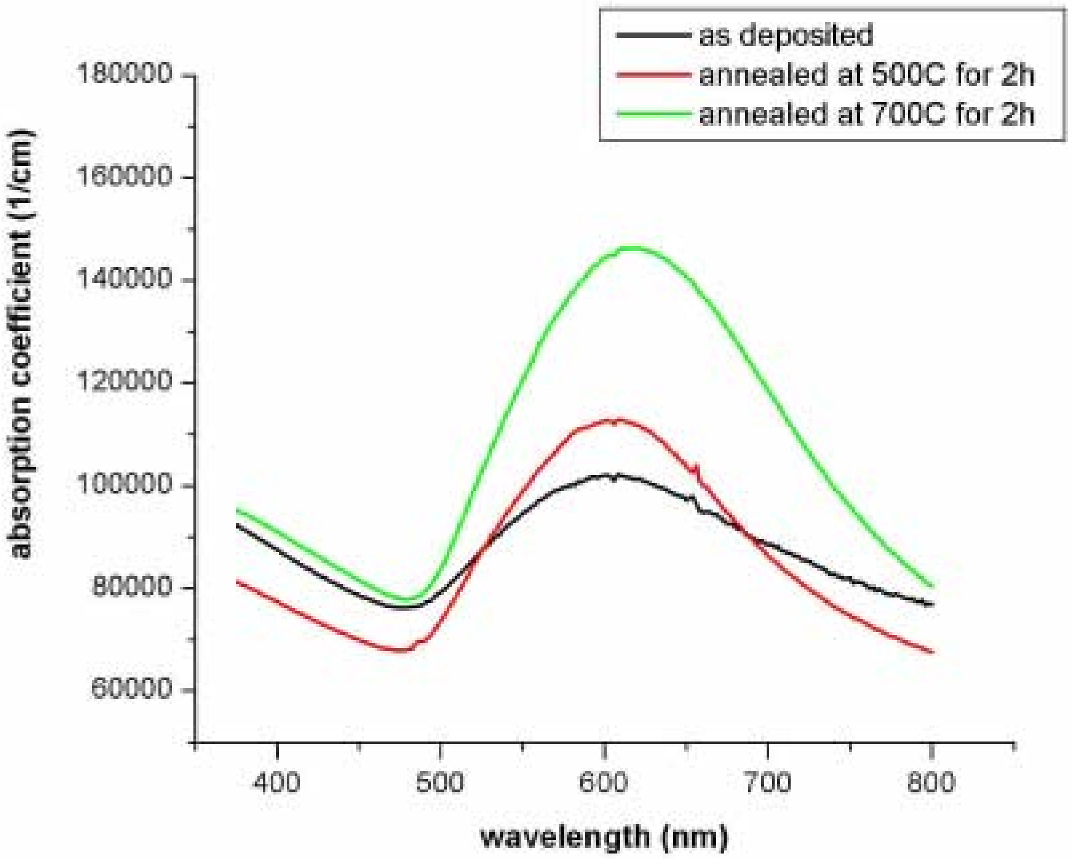


Deposition Parameters

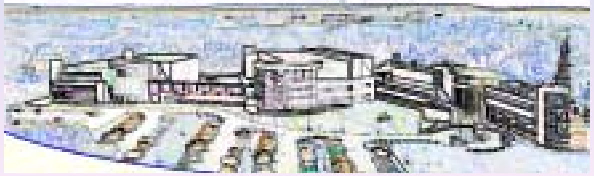
- Pressure: 5mTorr
- Ar flow: 5sccm
- RF Power: 300Watts
- DC Power: 30Watts
- Deposition time: 10min.
- Substrates: glass/sapphire/silicon
- Thickness: 100nm



Off-line Optical Analysis of Films



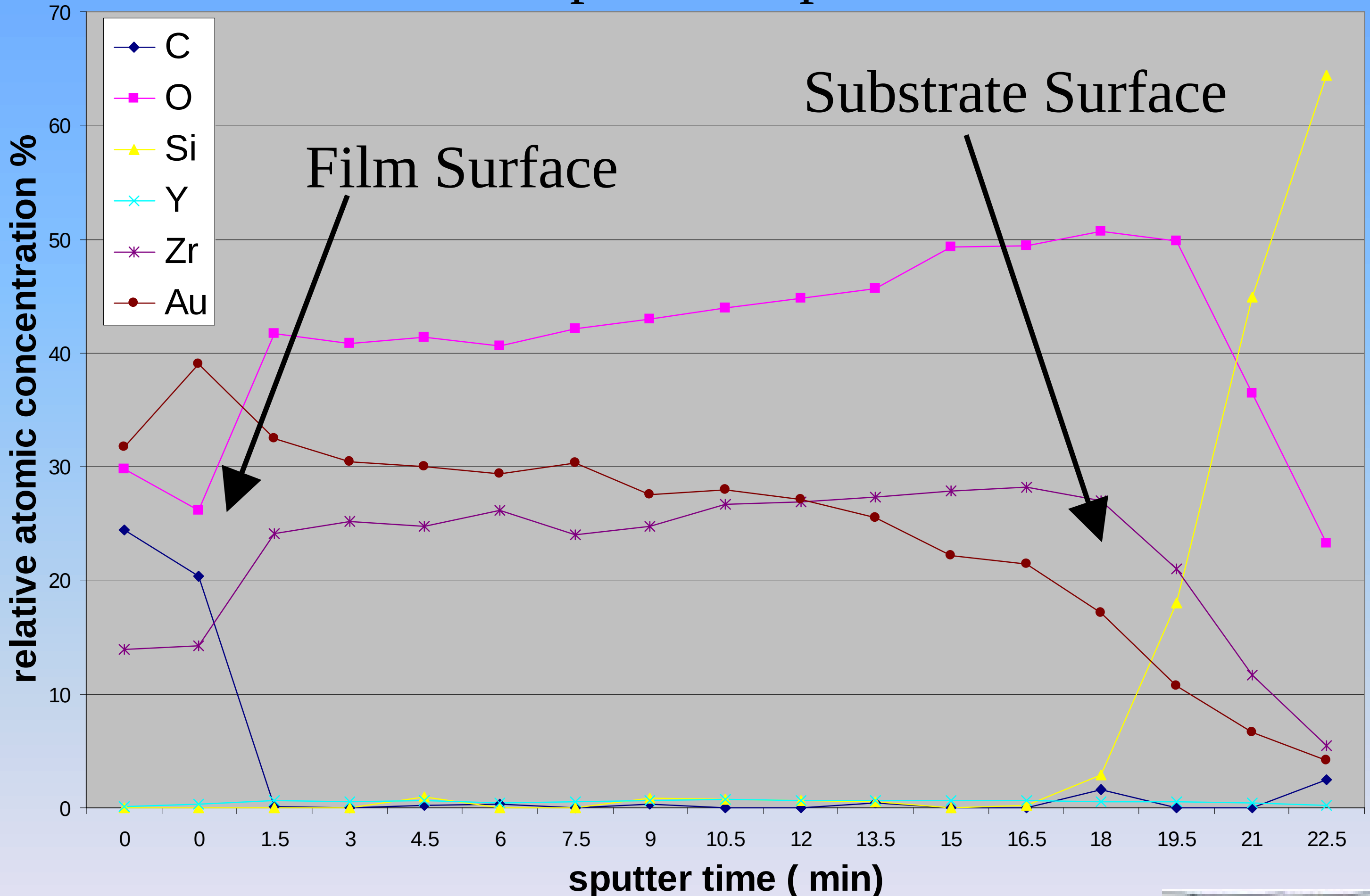
- 100nm Film on Sapphire
- Analyzed using an Hewlett Packard Spectrometer
- Annealed under Argon and then subsequently analyzed
- Intensity increase and shift to larger wavelengths indicates nanoparticle growth



X-ray Photoelectron Analysis

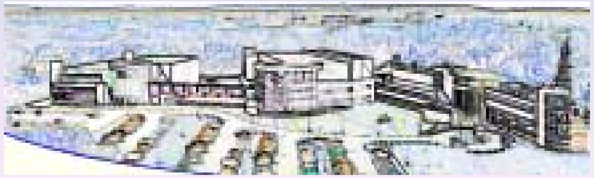
UNIVERSITY AT ALBANY
STATE UNIVERSITY OF NEW YORK

Nanocomposite Depth Profile



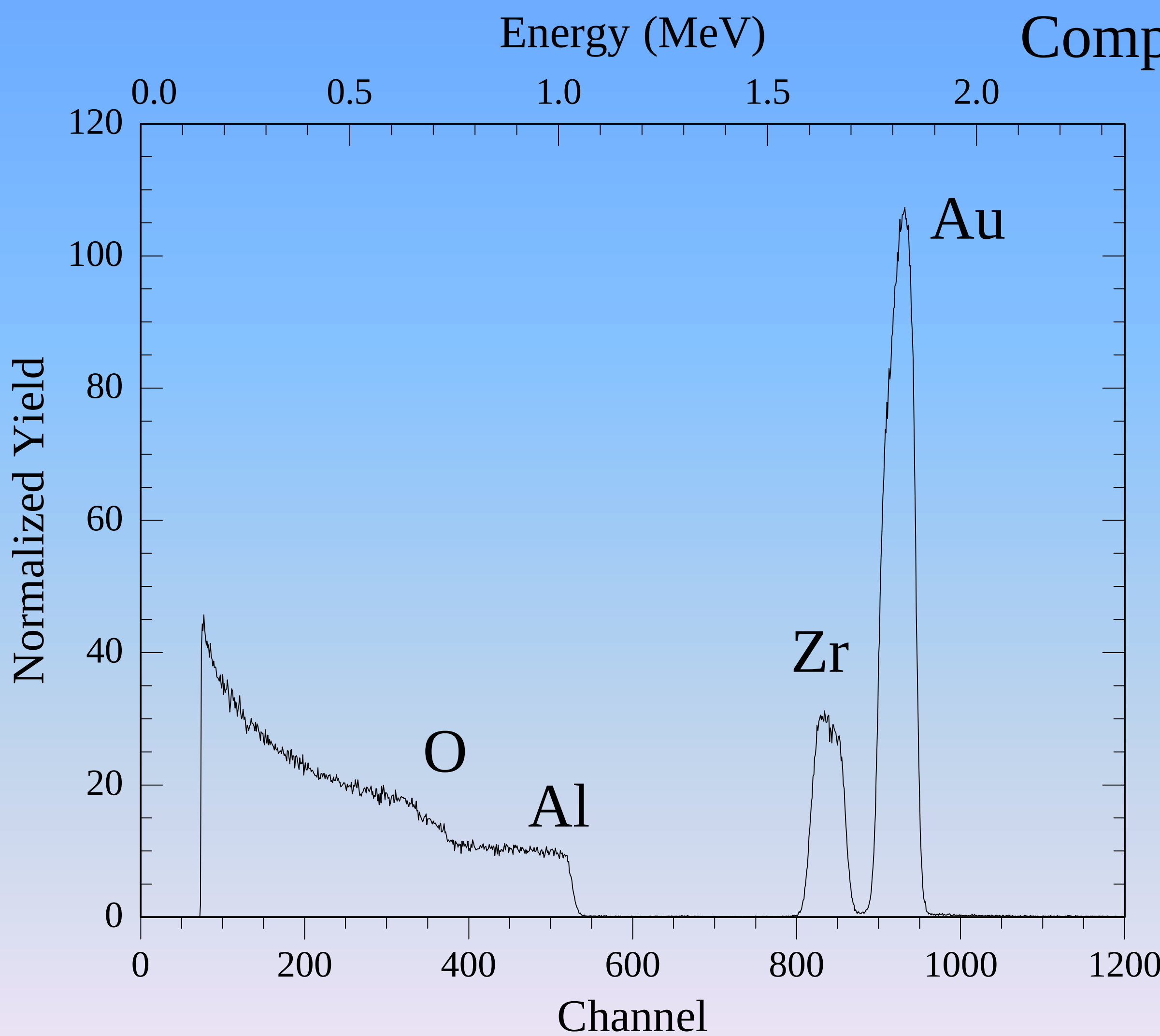
- 100nm thick film, as deposited on silicon
- Carbon surface contamination
- Film composition is uniform to 10%

School of NanoSciences and NanoEngineering

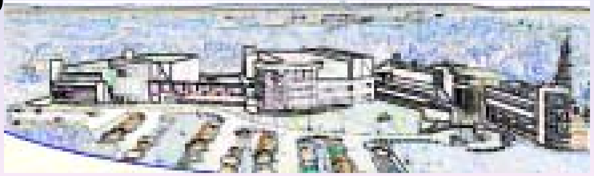


Rutherford Back Scattering

Film Uniformity and Compositional Analysis



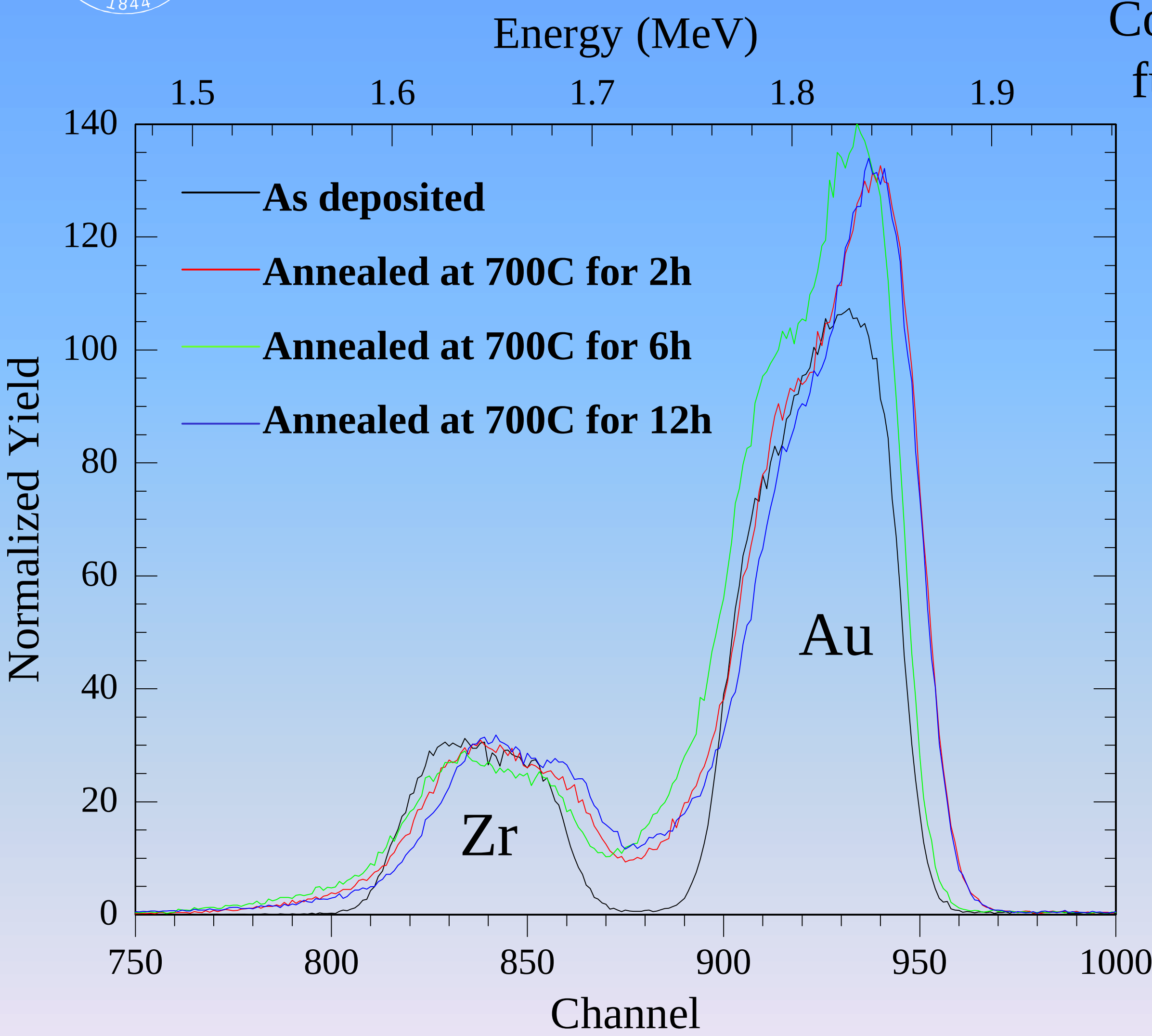
- 100nm film, as deposited on sapphire
- FWHM of both Au and Zr peaks are the same. Au and Zr are uniformly deposited throughout the film.



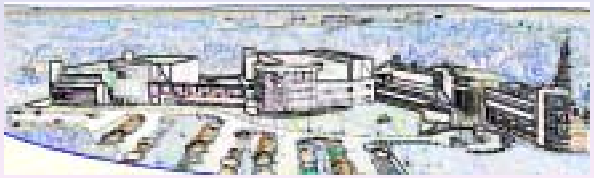
Rutherford Back Scattering

UNIVERSITY AT ALBANY
STATE UNIVERSITY OF NEW YORK

Film Uniformity and Compositional Analysis as a function of off-line anneal

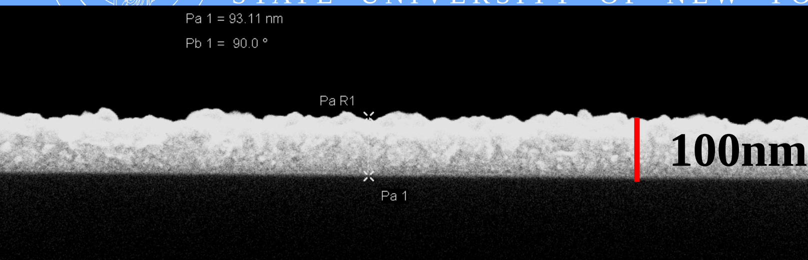


- 4 samples same recipe
  - -300W RF, 30W DC
  - -100nm film
- Films are uniform after anneal
- No high Z contamination

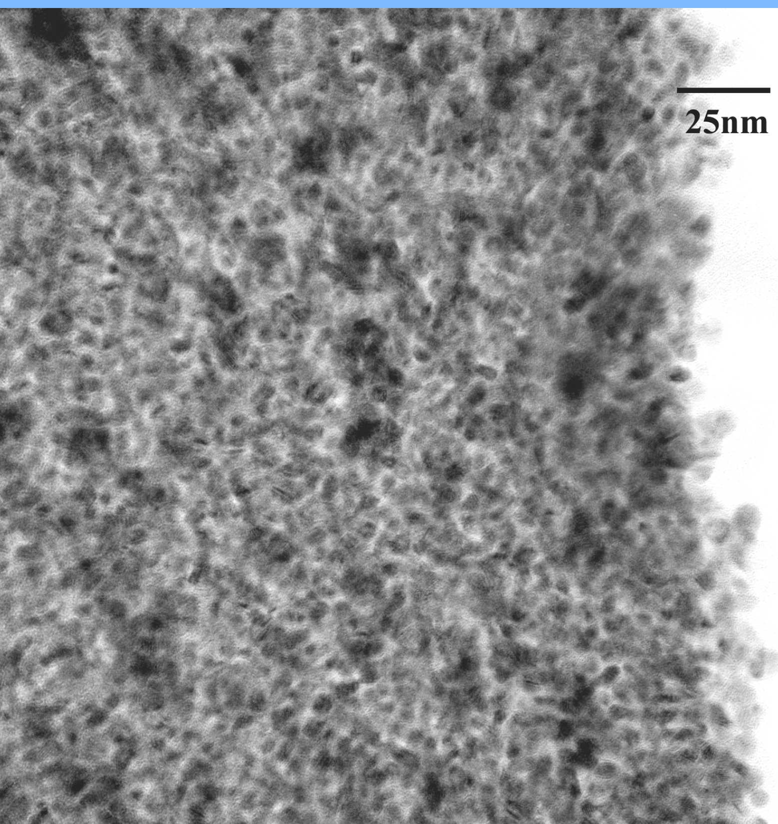


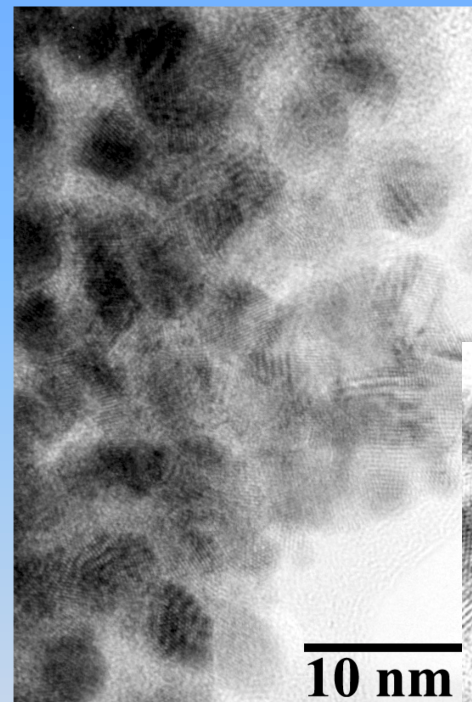
UNIVERSITY AT ALBANY
STATE UNIVERSITY OF NEW YORK

SEM/TEM Analysis of Films

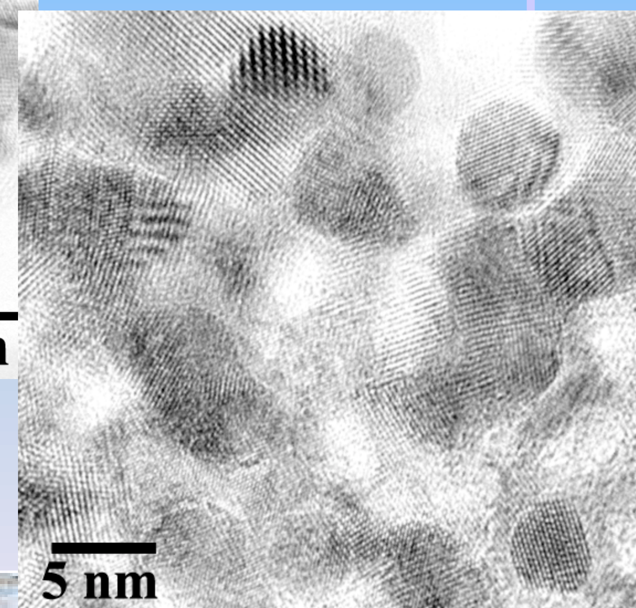


- SEM cross section of 100nm film on glass





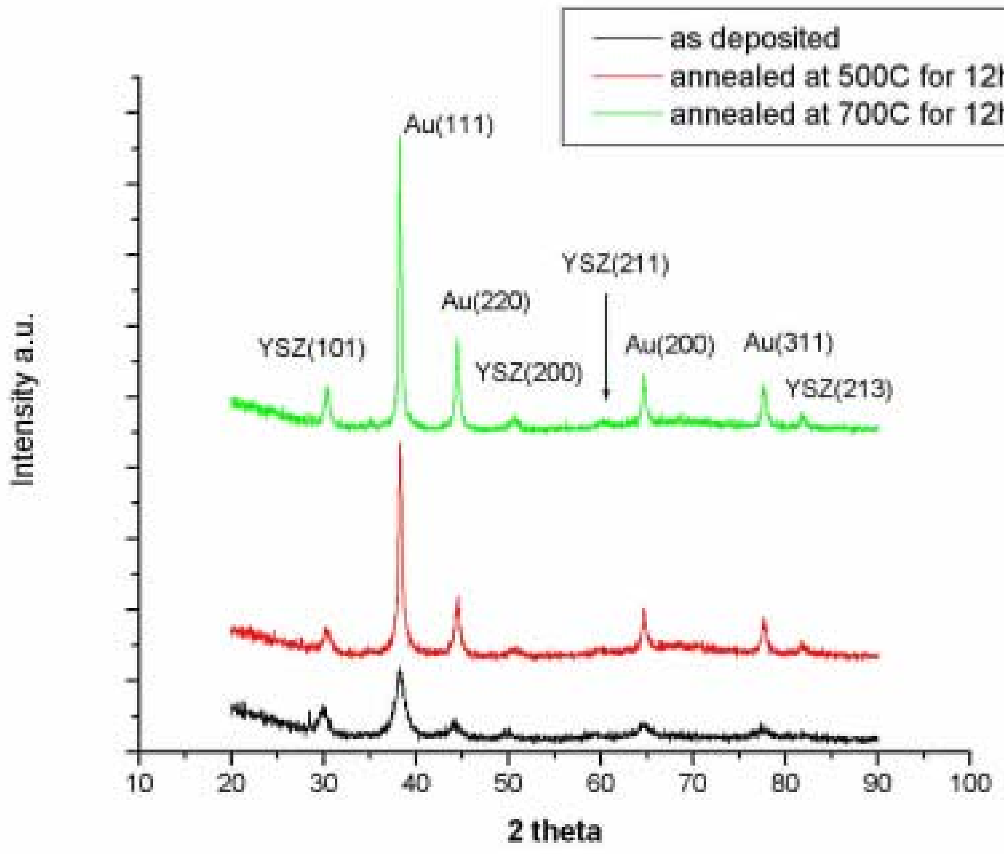
- TEM analysis of an as deposited 30nm film
- Sized 50 particles: 4.7nm±0.9nm



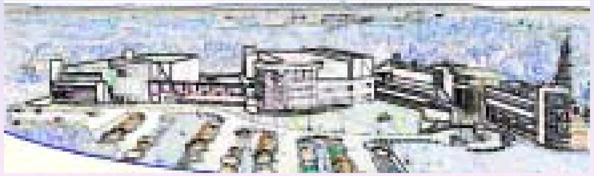
- Annealed sample to 500°C for 2 hrs
- Sized 50 particles: 5.2nm ±0.7nm

X-ray Diffraction Analysis

UNIVERSITY AT ALBANY
STATE UNIVERSITY OF NEW YORK



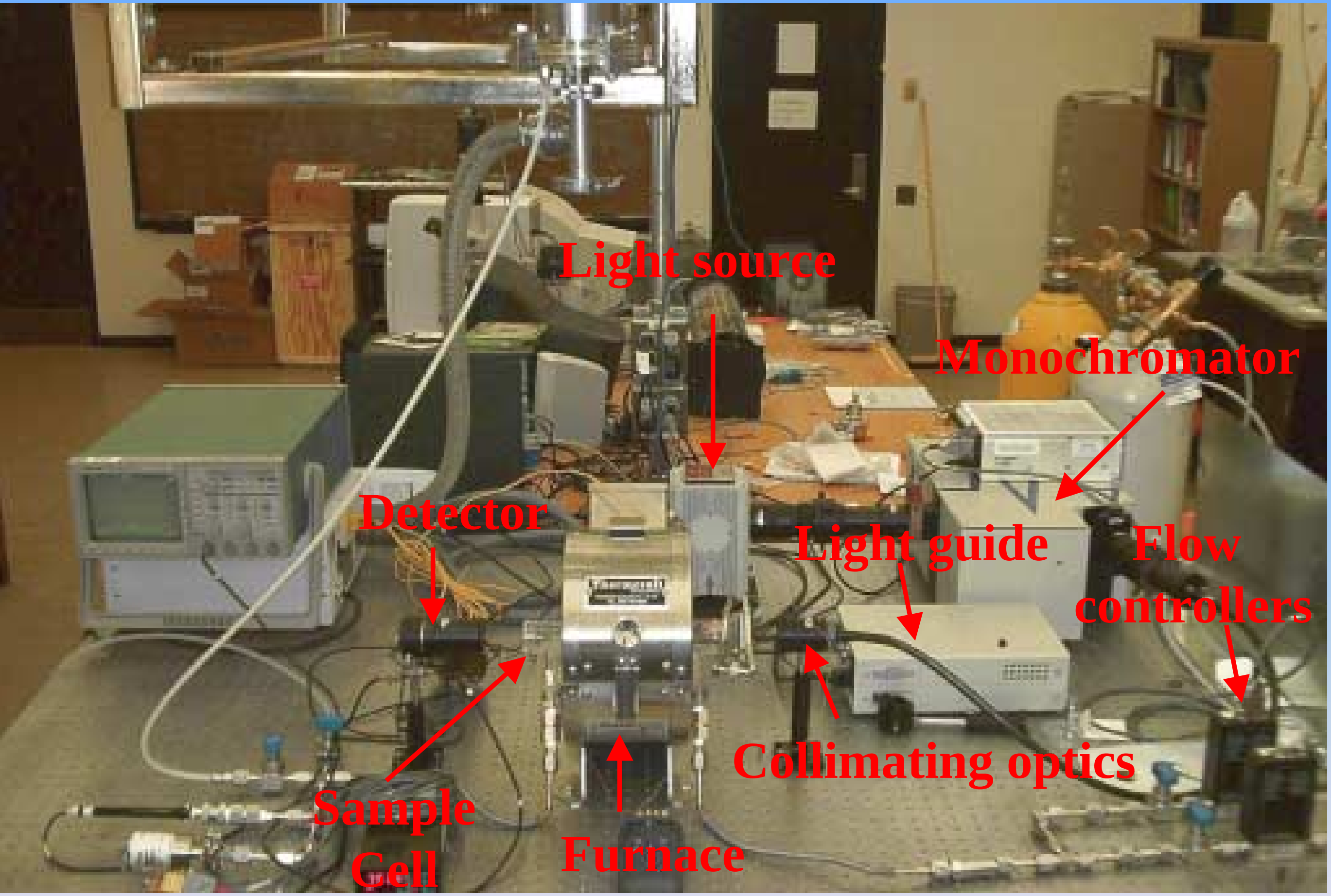
- Crystal character increases with thermal anneal
- Grain size analysis is in progress



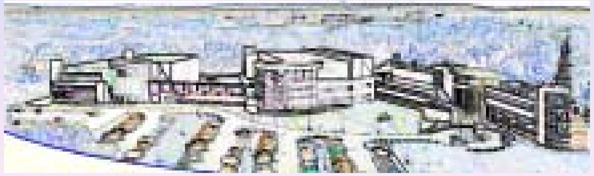
UNIVERSITY AT ALBANY
STATE UNIVERSITY OF NEW YORK

High Temperature Optical Bench

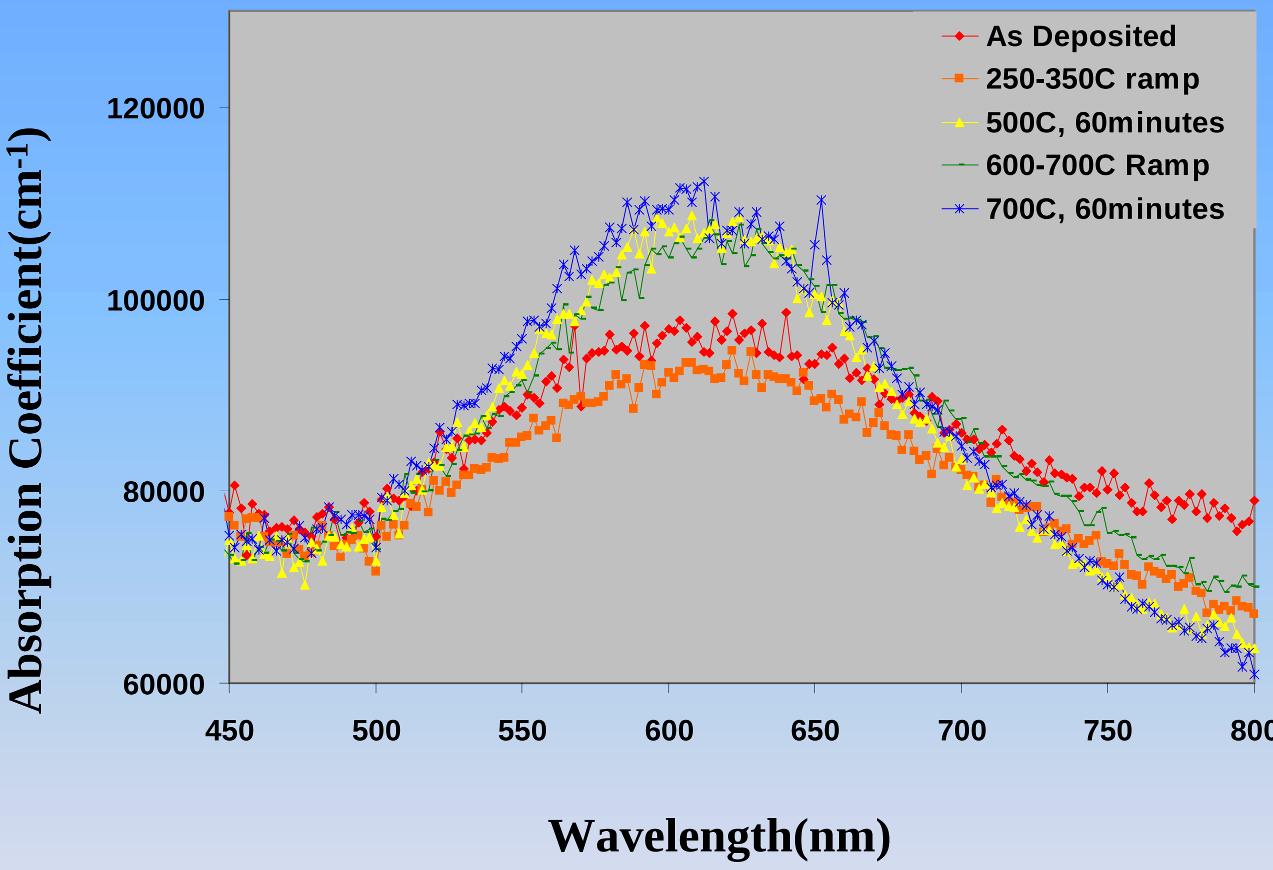
In-situ optical analysis(absorption) of nanocomposite



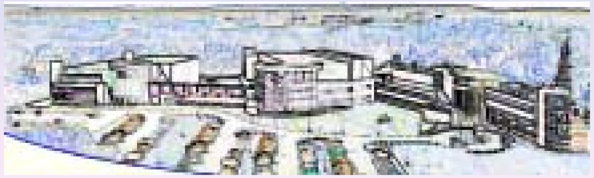
- 5J Xe flashlamp
- Oriel MS257 monochromator
- Si photodiode
- Oven: up to 1200°C
- Quartz sample cell
- Macor sample holder
- 1sccm gas flow
  - N_2, 100ppm CO in N_2, air



In-situ Optical Analysis of Nanocomposite Films

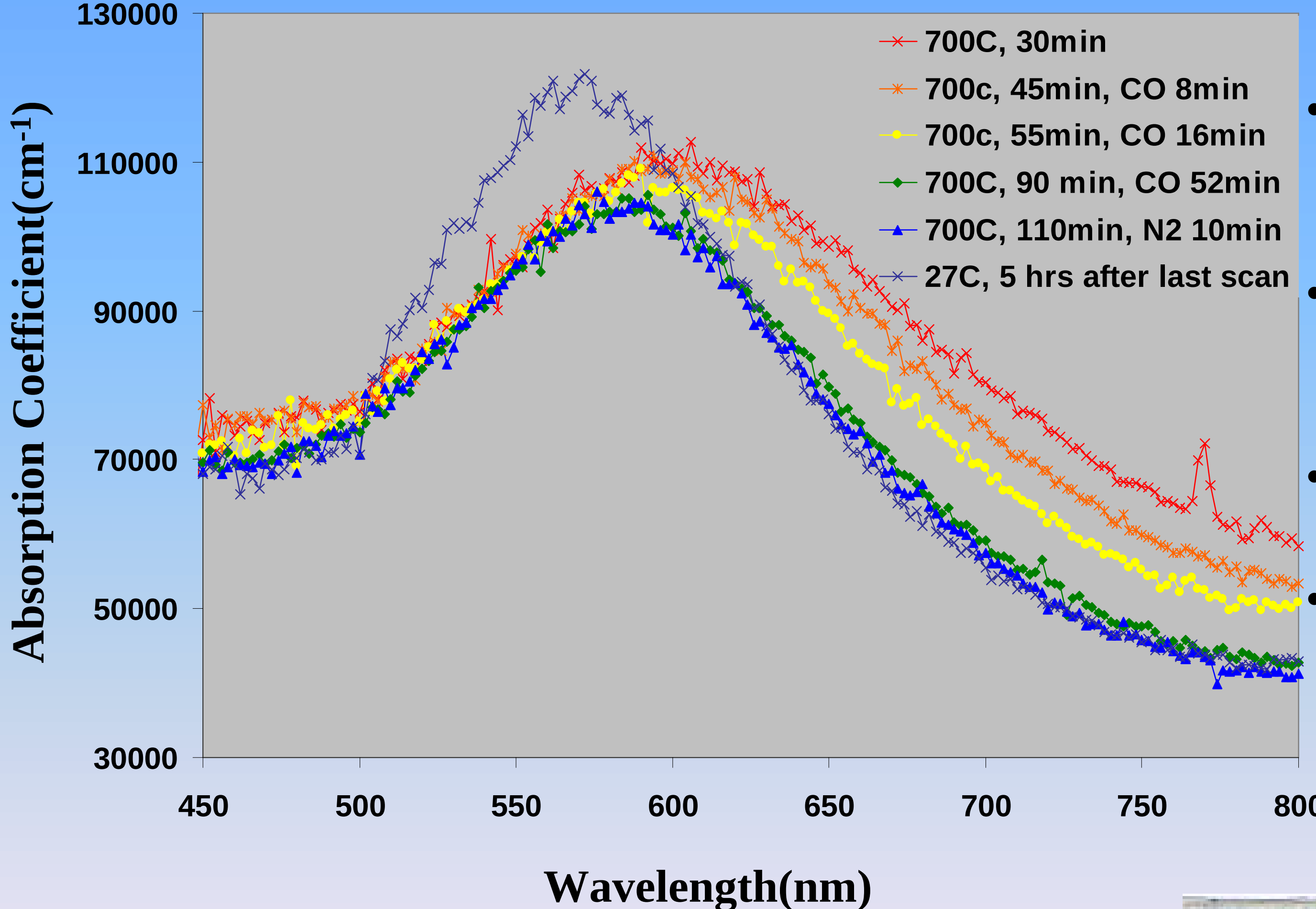


- 100nm film on sapphire
- 1L/min of nitrogen
- Initial decrease in intensity
- Blue shift and increase in the SPR band
- FWHM decrease
- Decrease in dielectric
- Increase in particle numbers



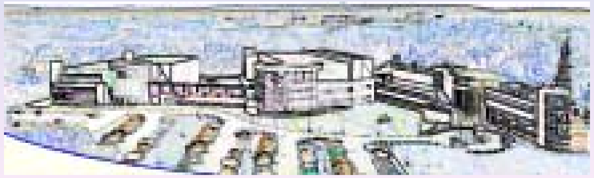
UNIVERSITY AT ALBANY
STATE UNIVERSITY OF NEW YORK

In-Situ Analysis as Function of Temperature and CO Exposure

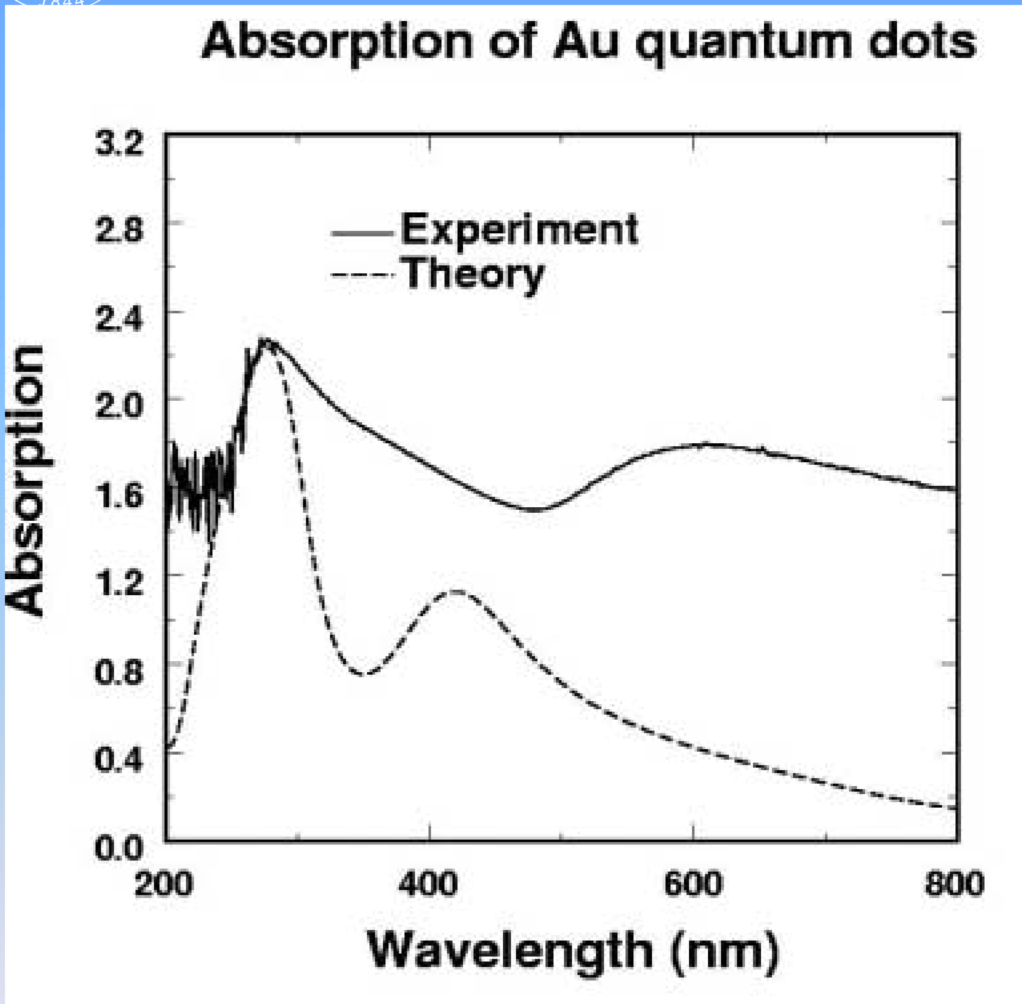


- Film exposed to 100ppm of CO in N_2
- Within our time resolution(7min) see difference in spectra
- Blue shift and narrowing of red tail

- Not reversible with N_2 flow
- Blue shift and increase in intensity upon cooldown



Simple Theory of Classical Scatterers in a Thin Film

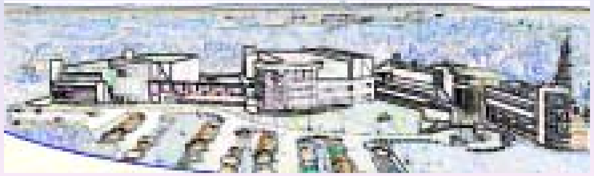


- Simplest starting point: classical spherical scatterers with bulk gold properties.
- Nanoparticles in dielectric thin film.
- Results qualitatively correct.
- Quantum polarizability will improve results.
- Dielectric surroundings and geometry (thin film) have important effect on absorption.

Conclusions

- We are able to deposit nanocomposite thin films of Au nanoparticles in a YSZ matrix
- We have developed a high temperature in-situ absorption cell system for optical analysis of materials

- SPR Bands are thermally stable once reach given temperature
  - Do see a blue shift and intensity increases upon cooldown, but repeated heat treatments to working temperature produces repeatable bands
- Have shown that SPR bands are sensitive to 100ppm of CO in nitrogen



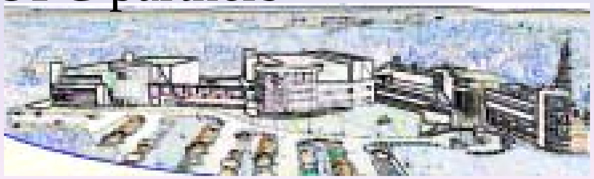
Future Work

- Optimize deposition routine for maximization of SPR signal and narrow bandwidth
- Perform experiments in presence of O_2 and H_2O
- Calibrate response as function of CO concentration(1ppm to % levels)
- Extend to deposition and testing of Pd and Pt nanocomposites(perform testing against CO and H_2)
- Theoretical calculations will be used to help determine if response is due to nanoparticle (size or shape) or to modifications in surrounding dielectric.

Future Phases

- Integrate in-situ FTIR measurements to probe mechanism
- Improve time resolution to seconds time scale by modifying optical bench to include CCD detector

- Industrial outreach through current and future SOFC partners



Acknowledgements

George Sirinakis(Ph.D student)

Dr. James Raynolds(SNN professor)

Dr. Kathleen Dunn(SNN professor)

DOE-NETL DE-FG26-02NT41542